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THE EFFECT OF HIGH TEMPERATURES
ON THE STABILITY AND IGNITION PROPERTIES OF
COMMERCIAL TRIARYL PHOSPHATE FLUIDS

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ABSTRACT

Commercial triaryl phosphate ester (TAP) fluids were exposed at temperatures of 200° to $500^\circ F$ to air of various relative humidities. Hydrolysis, oxidation, and degradation of the esters were followed by titration of the acidic residues and distillates, by measurement of oxygen consumption, and by viscosity measurements of the residues respectively. The resultant residues and distillates contained acids, phenols, tars, and water. The concentrations of these products and the viscosities of the residues exposed at $300^\circ F$ and above increased significantly as the temperature, relative humidity, and exposure time were increased.

The ignition temperatures (spontaneous ignition, flash and fire points) of the fluids did not decrease significantly, even though extensive degradation of the fluid had occurred at $300^\circ F$ and above.

PROBLEM STATUS

AUTHORIZATION

THE EFFECT OF HIGH TEMPERATURES
ON THE STABILITY AND IGNITION PROPERTIES OF
COMMERCIAL TRIARYL PHOSPHATE FLUIDS

INTRODUCTION

Triaryl phosphate esters (TAP fluids) have been used for many years as hydraulic fluids, lubricants, lubricant and fuel additives, and corrosion preventive fluids. Commercially these fluids are mixtures of esters of orthophosphoric acid and phenol or substituted phenols and are frequently referred to as tricresyl phosphates. These mixtures have properties which enable them to function acceptably as lubricants and hydraulic fluids in many applications.

During the past few years the use of phosphate esters by the Navy has grown rapidly (1). These fluids are in common use in such shipboard applications as the hydraulic equipment for deck-edge elevators and air compressors. The property of the TAP fluids which makes them particularly attractive for use is their resistance to ignition and combustion. A military specification entitled "Hydraulic Fluid, Fire Resistant" (2) covers the requirements which must be met by phosphate ester fluids. Several rather severe demands for resistance to inflammability are included in this specification.

Although the phosphate ester fluid is very fire resistant in its original form, it is possible that should the lubricant in some manner enter a high-pressure system and become lodged therein, it would be subjected to conditions which would probably lead to chemical degradation of the lubricant. It then becomes important to know the resistance to combustion of the breakdown products, especially of the residues in this instance. Since the identity of the products of the chemical breakdown of triaryl phosphates under such conditions apparently is not very well known, a study was begun at this Laboratory to learn more about the materials obtained when these esters are subjected to the various pyrolytic, hydrolytic, and oxidative conditions of the sort prevailing in air compressor systems.

Results of an extensive study of the toxicity of phosphate ester fluids has been published by the Bureau of Medicine and Surgery (3-5) and additional research by the Navy Toxicology Unit of this Bureau is in progress. It is likely that the current study of degradation products of the TAP fluids can contribute to the appreciation of the possible toxicity hazards of these materials under conditions of use.

In addition, an interest by the Navy in the acidity and corrosivity of the degradation products has been manifested from time to time.

The TAP fluids were exposed to temperatures ranging from $200°$ to $500°F$ and both the residues and distillates were studied. The effects of moisture on fluid stability were observed by varying the relative humidity of the air to which the samples were exposed. Acidity and oxygen uptake were measured at intervals during the treatment of the fluid, and viscosity was measured at the end. Spontaneous ignition temperatures and flash and fire points of the residues were also determined.

MATERIALS AND PROCEDURES

TAP Fluids

Three commercial TAP fluids, designated A, B, and C, were studied. Fluids A and B were designated by their manufacturer to be phosphate ester base fire-resistant hydraulic fluids and synthetic lubricants of controlled viscosity. Fluid C was primarily a corrosion-resistant preservative and not an operating lubricant for compressors.

By means of elemental analyses (oxygen by difference), the empirical formulas of fluids A and B were calculated to be $C_{23}H_{25}PO_4$ (C = 69.84%, H = 6.36%, P = 7.85%, and O = 15.95%) and $C_{25}H_{29}PO_4$ (C = 71.05%, H = 7.10%, P = 7.76%, and O = 14.09%) respectively. These are equivalent to molecular weights of 396 and 424.

Since the phosphoric acid ester of cresol would have a molecular weight of 368, it is evident that these mixtures must contain substituted phenols of higher molecular weight, including the equivalent of two and even three methyl groups per ring.

Thermal Exposure Treatment

The apparatus and conditions used for thermally stressing these fluids were as follows: a charge of about 250 ml of TAP fluid in a 500-ml round-bottom flask was maintained at the required temperature by means of a heating mantle and controlled to $\pm 10^0$F. Air of controlled relative humidity (0%, 9%, and 93% R.H. at room temperature) was bubbled through the fluid at 200 ml/min for the duration of the heat treatment. The air, upon leaving the flask, passed successively through a water condenser, an ice-water trap, and a dry-ice-acetone trap. The residues in the flask and the distillates which were collected in the traps were examined by various means.

Oxygen Analysis

In some cases changes in the oxygen content of the air as it passed through the reaction system were determined by means of a Beckman Model F-3 Oxygen Analyzer.

### Acid Titrations and pH Measurements

Measurements of pH and titrations for acidity were made using a Beckman Model H2 pH Meter. The aqueous extracts of the residues were titrated using standard solutions of alcoholic KOH. The untreated phosphate esters and the residues were titrated for acidity using a special titration solvent and a standard alcoholic KOH solution, both prepared according to ASTM Method D664 (7).

Titrations of the TAP residues gave two distinct inflection points on each titration curve similar to that obtained with orthophosphoric acid. These inflection points were measurable even at low concentrations (Fig. 1).

Detection of Phenols

Qualitative tests for phenols were made on the aqueous extracts of the residues and distillates by noting the decolorization of dilute potassium permanganate solution or the color changes of a ferric chloride solution.

Fig. 1 - Titration of triaryl phosphate ester fluid r e s i d u e after exposure at 500°F for 24 hours with airflow of 200 ml/min at 93% R.H. at room temperature
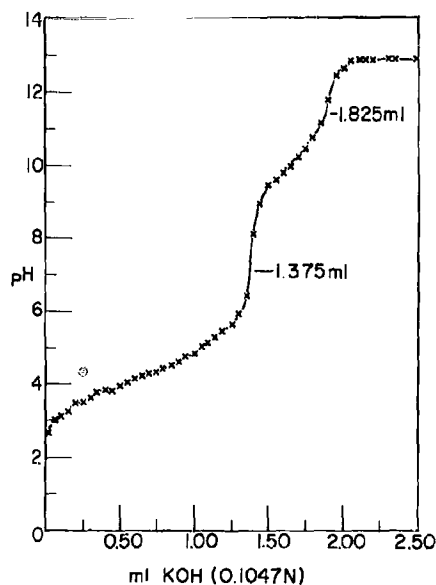
Analyses of the phenolic oil mixtures from the distillates by gas chromatography were made using a Perkin-Elmer Model 154 Vapor Fractometer. A column containing isodecyl phthalate ester on Chromosorb was used at 180°C.

Acid Titration in Presence of Phenols

Phenol and phenolic homologs are produced during the thermal degradation of TAP fluids. In order to examine the effect of phenolic compounds on the titration, aqueous solutions of phenol and phosphoric acid were titrated separately and in a mixture of the two. In each case, the initial volume of the aqueous solution titrated was 100 ml. In Fig. 2, curve A resulted from titration of a 0.005M solution of phenol and curve B from a 0.005M solution of phosphoric acid. The curve in Fig. 3 resulted from a solution of both phenol and phosphoric acid. The titers at the inflection points obtained in Fig. 3 were in good agreement with those obtained from curve B in Fig. 2 in spite of a significant decrease in the magnitude of the pH change at the second inflection point caused by the phenol. It is interesting that lowering of the pH and flattening of the titration curve did not obscure or distort the inflection point unduly. It is therefore possible to determine the acid content of the residues in the presence of phenols in which the phenol concentration is as great as that of the acid.

Viscosity Measurements

Kinematic viscosities were determined at 100°F by ASTM Method D445 (8) using Cannon-Fenske reverse flow type viscometers.

Spontaneous Ignition Temperature

The spontaneous ignition temperature (SIT) in air, of both untreated and treated samples was determined by the recently proposed method of the Bureau of Mines (9) as a modification of ASTM procedure D286-30. Ignition temperatures were determined by (a) injecting
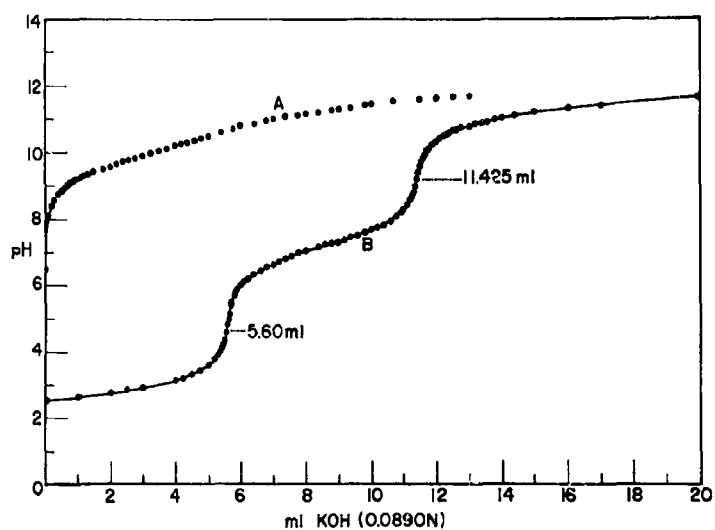
Fig. 2 - Titrations of aqueous phenol and
phosphoric acid: A - phenol, ca. 0.005M;
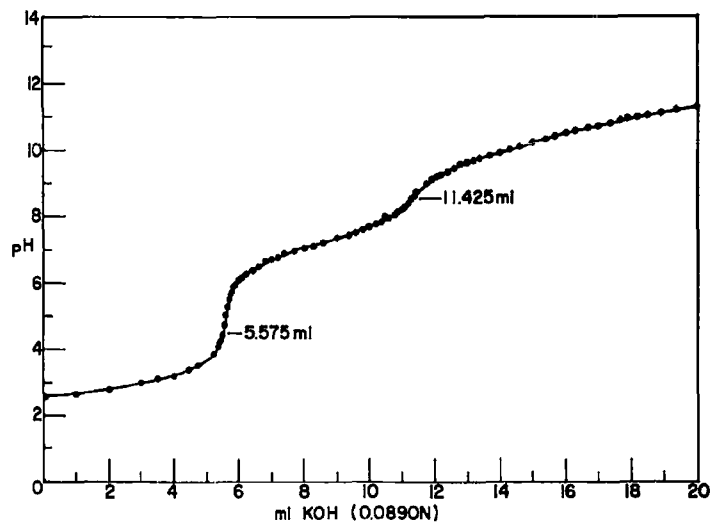B - phosphoric acid, ca. 0.005M

Fig. 3 - Titration of an aqueous solution of phenol and
phosphoric acid (0.005M concentration of each)

small measured quantities (about 0.1 ml) of the test sample into the flask by means of a hypodermic syringe or medicine dropper in the case of viscous samples, (b) observing occurrence of ignition, and (c) noting lowest temperature at which spontaneous ignition occurs as the SIT.

Flash Point and Fire Point

The Cleveland Open Cup (C.O.C.) Flash and Fire Point Tests (10) were used to determine these properties of the residues. Because of the possible toxicity hazard of working with these materials and their degradation products, all the ignition and combustion tests were made in a well-ventilated fume hood. The moving air may have caused a slight increase of a few degrees in the observed flash and fire points over those which might be obtained in perfectly quiet air.

RESULTS

Samples of fluids A, B, and C were subjected to thermal exposure at various temperatures and times as listed in order of severity of treatment in Table 1. A more detailed study of fluid A including variations in relative humidity is given in Table 2. At the end of each run, and in some cases at intervals during the run, portions of the distillate and residue were taken for examination by various means.

Distillates

In all cases, an odor reminiscent of phenols was strongly evident in the air stream even downstream of the cold traps. A positive qualitative test for phenols was obtained in the condensates collected in the traps. Usually a small amount of liquid distillate was collected in the traps as indicated in Tables 1 and 2. The distillates consisted of aqueous and oil phases. An oil phase distillate from a sample of fluid A treated at 500°F for 24 hours (with airflow of 200 ml/min at 9% R.H. and room temperature) was examined by gas chromatography. More than 85% of this particular distillate was comprised of at least six different phenols. Their peaks were compared to observed relative retention times of known materials. Phenol, o-cresol, and a mixture of m- and p-cresols were identified, the other two phenols were not. The aqueous distillates from TAP fluid A were titrated for acidity (Fig. 4) and results are shown in Table 2.

Appearance and Viscosity of Residues

The appearance of the residues depended greatly on the temperature and time of exposure. The samples treated at 400° and 500°F became black within 24 hours and the 500°F samples became tarry. Samples treated at 300°F showed slight darkening in 72 hours, but became a black, viscous liquid in three weeks, and a brittle solid in five weeks. The sample treated at 200°F showed only a slight change in appearance after six weeks. Viscosity changes are shown in Table 3.

Acidity of Residues*

Acidity data are given in Tables 1 and 2. In these tables, the quantity of acid reported in the case of treated samples is that of the acid actually produced during thermal exposure.

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*In this report, acidity of the residues is expressed in terms of milliequivalents of base per gram of residue (meq/g). Total acidity (H_T) is based on titration to the second inflection point on the curve and is equal to the sum of the acidities of the strongly ionized H_A and the more weakly ionized H_B.

Table 1
Thermal Exposure of TAP Fluids
(Air Flow at 9% R.H. at Room Temp)

TAP Fluid	Thermal Exposure		Residues								Distillates		
			Acidity (meq/g)					Acid Yield* (%)					
	Temp (°F)	Time (hr)	Total $[H_T]$	To 1st H^+ $[H_A]$	To 2nd H^+ $[H_B]$	Monoacid§ $[H_A R_2 PO_4]$	Ratio $[H_B]/[H_A]$	$[H_A]$	$[H_B]$	$[H_A R_2 PO_4]$	Aqueous† (ml)	Oil‡ (ml)	Total (ml)
A	Untreated	-	0.0004	0.0004	-	-	-	-	-	-	-	-	-
	300	72	0.0085	0.0044	0.0041	0.0003	0.93	0.18	0.16	0.01	1	0	1
	400	24	0.0395	0.0219	0.0176	0.0043	0.80	0.88	0.70	0.16	2	4	6
	500	24	1.61	1.32	0.29	1.03	0.22	52.8	11.60	41.2	2	5	7
B	Untreated	-	0.0005	0.0005	-	-	-	-	-	-	-	-	-
	300	72	0.0132	0.0074	0.0058	0.0016	0.78	0.30	0.25	0.061	2	0	2
	500	24	1.33	1.14	0.19	0.95	0.17	48.3	8.05	40.3	3	4	7
C	Untreated	-	0.2254	0.0728	0.1526	-	-	-	-	-	-	-	-
	500	24	2.36	1.52	0.85	0.67	0.56	-	-	-	0.5	5	5.5

*Based on theoretical complete hydrolysis.
†Chiefly H_2O.
‡Chiefly Oil.
§Concentration of monohydrogen diaryl phosphate derived numerically from $[H_A] - [H_B]$.

Table 2
Thermal Exposure of Fluid A
(Air Flow at 93% R.H. at Room Temp)

| Thermal Exposure | | Residues | | | | | | | | Distillates | | | | |
| | | Acidity (meq/g) | | | | | Acid Yield* (%) | | | | | | | |
Temp (°F)	Time (wk)	Total [H_T]	To 1st H⁺ [H_A]	To 2nd H⁺ [H_B]	Monoacid† [$H_A R_2 PO_4$]	Ratio [H_B]/[H_A]	[H_A]	[H_B]	[$H_A R_2 PO_4$]	Aqueous (ml)	Oil (ml)	Total (ml)	Aqueous Acid (meq/ml)	Distillate (pH)
Untreated	-	0.0004	0.0004	-	-	-	-	-	-	-	-	-	-	-
200	2	0.0129	0.0071	0.0058	0.0013	0.82	0.28	0.23	0.05	67	Trace	67	0.030	2.8
200	4	0.0178	0.0114	0.0064	0.0050	0.56	0.46	0.26	0.20	126	Trace	126	0.004	3.5
200	6	0.0252	0.0181	0.0071	0.0110	0.39	0.72	0.29	0.44	188	Trace	188	-	3.8
300	1	0.0699	0.0495	0.0396	0.0099	0.80	2.0	1.6	0.40	-	-	-	-	-
300	2	0.330	0.223	0.106	0.117	0.48	8.9	4.2	4.7	-	-	-	0.071	2.6
300	2.5	-	-	-	-	-	-	-	-	83	12	95	-	-
300	3	1.50	0.879	0.626	0.253	0.71	35.2	25.0	10.1	-	-	-	-	-
300	4	3.92	2.30	1.62	0.68	0.70	92.1	64.6	27.5	-	-	-	-	-
300	5	-	-	-	-	-	-	-	-	167	24	191	0.052	2.4
500‡	1 day	1.73	1.43	0.30	1.13	0.21	57.2	12.0	45.2	2	3	5	-	-
500§	1 day	1.61	1.32	0.29	1.03	0.22	52.8	11.6	41.2	2	5	7	-	-
500¶	1 day	2.52	1.88	0.64	1.24	0.35	75.2	25.6	49.6	8	3	11	-	-

*Based on theoretical complete hydrolysis.
†Concentration of monohydrogen diaryl phosphate derived numerically from [H_A] − [H_B].
‡Air flow of 200 ml/min at 0% R.H. at room temperature.
§Air flow of 200 ml/min at 9% R.H. at room temperature.
¶Average of 3 runs at 93% R.H.
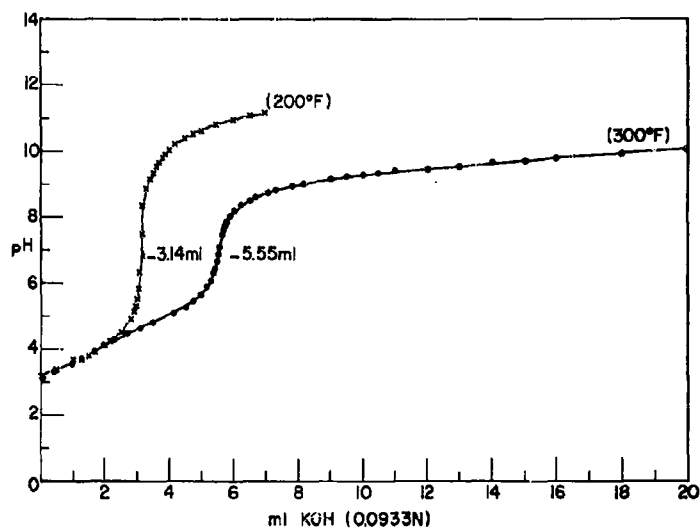
Fig. 4 - Titration of 10-ml samples of aqueous
distillates (fluid A)

Table 3
Viscosities of Residues After
Thermal Exposure
(TAP Fluid A)

Thermal Exposure		Viscosity at 100°F (Centistokes)
Temp ($^\circ$F)	Time	
As received	-	45.22
200*	6 weeks	46.78
300†	3 days	47.20
300*	5 weeks	Brittle solid
400†	1 day	52.04
500*	1 day	10,500

*Air flow of 200 ml/min at 93% R.H. at room
temperature.
†Air flow of 200 ml/min at 9% R.H. at room
temperature.

To obtain these figures for the treated samples, the quantity of acid initially present in the fluid before thermal exposure was subtracted in each case from the total quantity of acid found in the treated samples. A plot of acidities of TAP fluid A produced at 300°F (airflow of 200 ml/min at 93% R.H. and room temperature) against exposure time is given in Fig. 5

Fig. 5 - Acidities of triaryl phosphate ester fluid during degradation at 300°F (fluid A)
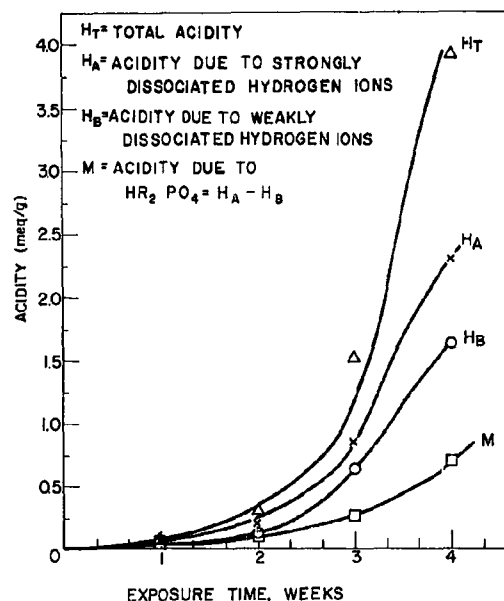
Titrations of the residues for acidity were very revealing. Assuming the acids to be due primarily to partial hydrolysis of the ester fluid under these conditions, the acid phosphates expected would be: monohydrogen diaryl phosphate ($H_A R_2 PO_4$), dihydrogen monoaryl phosphate ($H_A H_B RPO_4$) and phosphoric acid ($H_A H_B H_C PO_4$). Each of these acids would then contribute its share of hydrogen ions to a titration of such a mixture by a base. The first hydrogen (H_A) would be contributed by all three of these acids, and the second (H_B) by the di- and tri-hydrogen acids alone. The third hydrogen ion (H_C) would be contributed by phosphoric acid only but would not be a factor in this analysis due to its extremely weak ionization. By the method used, the concentration of the monohydrogen diaryl phosphate could be estimated. The equations for this procedure are:

$$[H_A] = [H_A R_2 PO_4] + [H_A H_B RPO_4] + [H_A H_B H_C PO_4]$$

$$[H_B] = [H_A H_B RPO_4] + [H_A H_B H_C PO_4]$$

$$[H_A] - [H_B] = [H_A R_2 PO_4]$$

In these equations, the bracket refers to the molar concentration of the species which it encloses. The calculated concentrations of the monohydrogen diaryl phosphate ($H_A R_2 PO_4$) are given in Tables 1 and 2.

Aqueous Extracts of Residues

To gain further information concerning the composition of the residues, a few aqueous extracts were examined to ascertain what water-soluble components were present in the residues. Phenols were detected in aqueous extracts of the residues in all cases by means of a qualitative color test with ferric chloride solution. The aqueous extracts were acidic (ranging in pH from about 1 to 2.8) containing both strong and weak acids and also free phosphate ion. The phosphate ion concentration of a water extract of the residue from fluid A after treatment (24 hours at 500°F, with airflow of 200 ml/min at 9% R.H. and room temperature) was determined to be 0.094 meq/ml by a colorimetric method (3). The concentration of hydrogen ion (first inflection point) in this extract was 0.098 meq/ml. This indicated that free phosphoric acid had formed by hydrolysis.

Oxygen Consumption During Thermal Exposure

In order to examine the role of oxidation in the degradation of TAP fluid, the oxygen content of the air was monitored by passing air from the last trap in the condensate train through warming coils and then through a magnetic-type oxygen analyzer. This was done for three samples of fluid A treated with an airflow of 200 ml/min at 93% R.H. and room temperature. At 500°F, the oxygen content of the air stream decreased from 21.0% to a minimum of 17.8% in two hours. After 8 hours, the oxygen content had risen to 20.5% to 20.8% where it remained until the end of the 24-hour experiment. A similar, but less pronounced oxygen uptake was observed at 300°F. At 200°F the rate of oxygen removal by the fluid was too small to be measured.

Thermal Exposure and Ignition Properties

Ignition data for SIT, flash, and fire points of the residues are given in Table 4.

Table 4
Ignition Properties of TAP Fluids After Thermal Exposure
(Air Flow at 9% R.H. at Room Temperature)

TAP Fluid	Thermal Exposure		SIT (°F)	C.O.C. Flash Point (°F)	C.O.C. Fire Point (°F)
	Temp (°F)	Time			
A	Untreated	–	1,025	515	700
	300	72 hr	1,025	500	700
	300*	1 wk	1,030	480	690
	300*	3 wk	1,005	460	540
	500	24 hr	980	–	–
B	Untreated	–	1,000	–	–
	300	72 hr	1,000	–	–
	500	24 hr	960	–	–
C	Untreated	–	1,040	–	–
	500	24 hr	1,040	–	–

*Air flow of 200 ml/min at 93% R.H. at room temperature.

DISCUSSION

The data in the tables and in Fig. 5 show the effects of thermal exposure on TAP fluids as a function of temperature, time, and relative humidity. In general the data show degradation of the TAP fluids and related increase in viscosity with increase in temperature, moisture content of the air, and duration of treatment. The degradation was indicated by darkening of the fluid, oxygen uptake, increased acidity, and by increased amount of distillate. The acidity and distillate data for three different TAP fluids (Table 1) showed this trend in all cases as a function of temperature and time of exposure. A more detailed study of a single TAP fluid (fluid A) is shown in Table 2.

Effect of Temperature on Stability of TAP Fluid

Exposure at 500°F (TAP Fluid A) - The stability of the TAP fluid at 500°F was poor under the conditions imposed upon it, e.g., with air passing through the fluid. After 24 hours the fluid was changed from a yellow liquid to a black semisolid which would have no value as a lubricant. The fluid was subjected to this high temperature because in certain air compressors some of the lubricant is exposed to surfaces at temperatures as high as 400° to 500°F. In addition, exposures at 500°F allowed certain accelerated studies to be made.

The data given in Table 2 for the acidity of TAP residue upon exposure at 500°F (air-flow of 200 ml/min at 93% R.H. and room temperature) can be used for comparison with other temperatures. The total acidity of 2.52 milliequivalents per gram (meq/g) of TAP fluid residue is made up of 1.88 meq/g of strong acid (H_A) and 0.64 meq/g of weak acid (H_B). These values correspond to 75.2% and 25.6% respectively of the theoretical hydrogen ion available assuming complete hydrolysis. Complete hydrolysis of an ester of molecular weight of 396 would yield 2.52 meq of each type of hydrogen ion per gram of ester.

In any case the amount of free acid found by titration shows that the TAP fluid is extensively degraded within 24 hours at 500°F. This is consistent with the high viscosity and general appearance of the residue. However, the total amount of phenolic oil distillate collected under these conditions was only 3 ml (see Table 2). This is a small fraction of the phenolic compounds which would be expected from such extensive hydrolysis as that indicated by the acid titrations, suggesting that most of the phenols remained in the residue, perhaps as polymeric material.

Exposure at 300°F (TAP Fluid A) - Examination of the TAP fluid residue in the reaction flask after exposure at 300°F (Table 2 and Fig. 5) showed that by the end of three weeks it had changed to a black viscous liquid. In five weeks it was a brittle solid.

The oily distillate in 2-1/2 weeks totaled 12 ml whereas the total acid in the residue after three weeks was 1.50 meq/g. This contrasts with the exposure at 500°F at which were obtained 3 ml of oil and a total acid value in the residue of 2.52 meq/g in 24 hours. The milder treatment at 300°F produced more phenolic distillate for a given amount of hydrolysis as measured by the total acid in the residues.

Figure 5 shows that a rapid increase in total acidity (H_T) begins after about two weeks at 300°F. It is observed that after four weeks the strong acid content (H_A) has reached 2.3 meq/g or 92% of that theoretically available. At the same time the weak acid (H_B) has also reached the high value of 1.6 meq/g or 65% of theory. The ratio of H_B/H_A of 0.70 is very different from the value of 0.35 obtained at 500°F after 24 hours. The value for H_B/H_A at 300°F was consistently high all during the experiment. Conversely the concentration of the monohydrogen diaryl phosphate at 500°F was high, 1.24 meq/g relative to 0.68 meq/g at 300°F.

The explanation for these data appears to be that as soon as one aryl group is hydro-
lyzed from the triaryl ester at 300°F there is a strong tendency for further hydrolysis of
the same molecule to occur. At 500°F the tendency for further hydrolysis of a given mole-
cule decreases after a single aryl group is removed.

Exposure at 200°F (TAP Fluid A) - TAP fluid A exposed for six weeks at 200°F (air-
flow of 200 ml/min at 93% R.H. and room temperature) was still a light amber color and
its viscosity had not changed appreciably (Table 3). Only a trace of oily distillate appeared
on the water in the traps (Table 2). It is noteworthy, however, that the aqueous distillate
was fairly acid. The results of the titration of biweekly samples of the TAP fluid (Table 2)
showed very little acid content had developed even after six weeks. It appears that the
TAP fluid should be usable at 200°F for more than six weeks.

Effect of Moisture Content of Air on Thermal Stability of TAP Fluid A

Experiments were run in which the triaryl phosphate fluid was heated for 24 hours
at 500°F and only the relative humidity of the air bubbled through the fluid at 200 ml/min
was varied (0%, 9%, and 93% R.H. at room temperature). The results of titrations of the
residues are presented in Table 2. Comparison of the total acidity values shows a large
overall increase in hydrolysis when air of 93% R.H. was used. The difference between dry
air and air of 9% R.H. was not discernible.

The acidity value to the first inflection point (H_A) measures hydrolysis of the first
aryl group of the ester fluid. From the H_A values at 93% R.H., it is estimated that an
average of 75% of the first aryl groups was hydrolyzed. This implied 20% additional
hydrolysis of first aryl groups due to increased moisture. However, hydrolysis of the
second aryl group, derived from H_B was approximately twice as great at 93% R.H.
(25.6%) as it was at lower relative humidity (11.6% ave). Additional moisture favored
more extensive hydrolysis of each molecule since the increase in H_B was proportionally
greater than the increase in H_A as the relative humidity of the air was increased. This
was shown more clearly by the ratios (H_B/H_A) of the measured acidities given in Table 2.

Types of Chemical Reactions Occurring During
   Thermal Degradation of TAP Fluids

During the course of these studies on the thermal degradation of TAP fluids exposed
to air, evidence accumulated which indicated that different types of chemical reactions
were occurring which contributed to the final products. Although hydrolysis appears to
be the major reaction, oxidation and polymerization occur to a large extent and some
pyrolysis is indicated. If the TAP fluid is made up of methyl-substituted phenols as
stated by the manufacturer, an average of 4 to 5 methyl groups per ester molecule is
indicated for a molecular weight of 396. This suggests a structure such as:

$$Ar'-O-\overset{\displaystyle O}{\overset{\displaystyle \uparrow}{P}}-O-Ar''$$
$$\underset{Ar'''}{\overset{|}{O}}$$
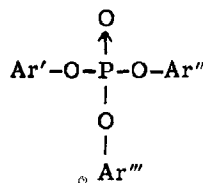
in which the aryl (Ar) groups are predominantly tolyls and xylyls. The manufacture of the
TAP fluid begins with a mixture of phenols which likely form mixed esters of many differ-
ent combinations. Chromatographic analysis of a hydrolyzate has indicated that at least
six different phenols are involved.

Oxidation - Oxidation was shown to play a significant role in the degradation of the TAP fluid. The most direct evidence was the fact that oxygen was removed from the air stream which bubbled through the fluid. It is significant that in these experiments the greatest rate of oxygen uptake occurred at a very early stage, whereas the more pronounced changes in acidity and viscosity were observed later. Results of related work at the U.S. Naval Engineering Experiment Station (6) were in accord with the findings at this Laboratory that oxygen is taken up during thermal degradation of TAP fluids.

Additional indirect evidence for the occurrence of oxidation was the fact that there was an increase in total weight of the system during thermal degradation which could not be explained by absorption of water carried by the air. Also the amount of water collected in the condensate traps and the calculated amount which must be necessary for hydrolysis of the phenols and acidic fragments indicates that much water is produced during degradation, some of which is probably an oxidation product.

Further indirect evidence is the fact that tritolyl phosphate was reported by others to be relatively stable at $536°F$ in an atmosphere of nitrogen with only a little increase in viscosity (11). This is contrary to the considerable change found in air with mixed triaryl phosphates.

Hydrolysis - There is no doubt that hydrolysis of the phosphate esters occurred during these experiments since phenols were collected in the distillates and were also proven to be in the residues. In addition, the presence of phosphate ions, the titer of the residues and the profiles of the titration curves strongly indicate that acid phosphates were produced by hydrolysis of the TAP fluids. The almost quantitative recovery by titration of the acid phosphate residues in some cases (e.g., Tables 1 and 2) indicates that hydrolysis occurs without significant loss of phosphate. This does not deny the prior oxidative attack on the phenolic portion.

In aqueous systems at lower temperatures, a number of aryl phosphates have been shown to hydrolyze completely (12-16).

Polymerization - Perhaps the strongest evidence for polymerization is the marked increase in viscosity found after thermal degradation of the TAP fluid. Polymerization of phenolic fragments is also indicated by the small amount of phenols found in the distillate in spite of the considerable hydrolysis shown by titration. If the phenols had remained unpolymerized they would have been collected in the distillate. This polymerization could also supply more water for further hydrolysis.

Pyrolysis - Pyrolysis to carbon was negligible since the black brittle solid residues resulting from extensive degradation yield a clear red solution upon refluxing with concentrated nitric acid. Carbon is insoluble in nitric acid and would have remained as insoluble particles. Pyrolysis to yield small molecules has not been investigated but most probably occurs to some extent.

Thermal Exposure and Ignition Temperatures

The ignition data (Table 4), for fluid A and residues imply that all three types of ignition show a gradual drop in temperatures as a result of both increase of exposure temperature and time, and that the drop in SIT was least. Fluid B also showed a drop in SIT as a result of thermal exposure, while TAP fluid C showed none. For fluid A over the three week period, the temperature drops were approximately $20°F$ for the SIT, $55°F$ for the flash point, and $160°F$ for the fire point. The greater change in the flash and fire points may be the result of thermal degradation of the original material to lower molecular weight fragments of higher volatility. Flash and fire points are partly a function of the vapor pressure of the material tested. These temperature drops, although they indicate a trend,

are relatively small when one considers that they are the result of so drastic a thermal treatment. In general, however, values obtained after three weeks of treatment at $300^{\circ}F$, and after 24 hours at $500^{\circ}F$ were still relatively high compared to the values for untreated petroleum oils. Ignition data from the literature for petroleum type lubricants and hydraulic fluids indicate a wide range of temperature values depending on the material, method, etc. These values range as follows (17-21): SIT - 466° to $700^{\circ}F$, flash point - 300° to $555^{\circ}F$, and fire point - 215° to $615^{\circ}F$. Because the TAP samples became extremely viscous after 24 hours at $500^{\circ}F$ and three weeks at $300^{\circ}F$, it became increasingly difficult to handle or sample the tarry residues. For this reason the tests were terminated after three weeks.

As has been discussed, phosphoric acid esters of mixed phenols and cresols break down at high temperature to fragments which would include free phenols and cresols.

The spontaneous ignition values for o-cresol and p-cresol were determined for comparison and were found to be $925^{\circ}F$ and $1025^{\circ}F$ respectively. These values compare well with the SIT data of the TAP fluids and this suggests that mixtures of phenols, cresols, and other methylated aromatic compounds formed upon thermal degradation of esters could account for the SIT values found for the phosphate ester fluids. For this reason, and because similar degradation probably occurs during the actual SIT determination of the TAP fluid, SIT values would not be expected to show significant changes as a result of thermal stressing. Therefore, SIT values would not be a good criterion of resistance to thermal degradation.

CONCLUSIONS

1. Degradation of the TAP fluid and the viscosity of the residues increased with temperature, moisture content of the air, and duration of treatment.

2. The hydrolytic effect of moisture was demonstrated by exposing samples of TAP fluid for 24 hours at $500^{\circ}F$ and varying only the relative humidity of the air. The concentration of the monohydrogen diaryl phosphate formed was approximately the same in each case, whereas the concentration of dihydrogen phosphates (including possibly phosphoric acid) was doubled with air of high relative humidity.

3. It was demonstrated that oxygen was taken up by the fluid at elevated temperatures. The maximum rate of oxygen acceptance occurred before extensive degradation of the fluid was observed.

4. The experimental data obtained thus far indicate that the degradation of the triaryl phosphate fluids under the conditions used proceeds via early oxidation followed by hydrolysis and polymerization. Pyrolysis to carbon was found to be negligible.

5. Although a drop in ignition temperatures of TAP fluids was noted, these depressions in SIT, flash, and fire points were relatively small and not very significant after so drastic a thermal treatment.

6. SIT values are not a good criterion of resistance to thermal degradation.

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of the residues exposed at 300°F and above increased significantly as the temperature, relative humidity, and exposure time were increased.

The ignition temperatures (spontaneous ignition, flash and fire points) of the fluids did not decrease significantly, even though extensive degradation of the fluid had occurred at 300°F and above.